PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 7/167

A1

(11) International Publication Number: WO 99/55648

(43) International Publication Date: 4 November 1999 (04.11.99)

(21) International Application Number: PCT/NL99/00245

(22) International Filing Date: 26 April 1999 (26.04.99)

(30) Priority Data:
1009014 28 April 1998 (28.04.98) NL

(71) Applicant (*for all designated States except US*): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): BOSMAN, Hubertus, Johannes, Mechtilda [NL/NL]; Wielewaalstraat 13, NL-6135 EN Sittard (NL). GROOTENDORST, Edwin, Jacco [NL/NL]; Ankersweg 57, NL-6123 AJ Born (NL). POSTMA, Leonardus, Hubertus [NL/NL]; St. Pieterstraat 101A, NL-6463 CX Kerkrade (NL). SMEETS, Theodorus, Maria [NL/NL]; Burg. Eussenstraat 6, NL-6181 BP Stein (NL).

(74) Agent: SCHELTUS, Irma; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR THE HYDROGENATION OF PHENYL ACETYLENE IN A STYRENE-CONTAINING MEDIUM WITH THE AID OF A CATALYST

(57) Abstract

The invention relates to a process for the hydrogenation of phenyl acetylene in a styrene-containing medium with the aid of a supported nickel catalyst with a nickel content of 10-25 wt.%. This process is by preference used for the hydrogenation of phenyl acetylene in a styrene-containing medium which contains more than 30 wt.% of styrene.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

9271WO

PROCESS FOR THE HYDROGENATION OF PHENYL ACETYLENE IN A STYRENE-CONTAINING MEDIUM WITH THE AID OF A CATALYST

The invention relates to a process for the hydrogenation of phenyl acetylene in a styrene-containing medium with the aid of a catalyst.

Styrene is often polymerized to polystyrene. In the styrene-containing medium which is used for this purpose, the phenyl acetylene causes undesirable side reactions during the polymerization, such as cross-linking of the polymer chains. It is therefore of importance to keep the phenyl acetylene content of the styrene-containing medium as low as possible.

The above-mentioned process for the hydrogenation of phenyl acetylene is known from JP-A-55,35368.

Said patent publication describes a process for the hydrogenation of phenyl acetylene in a mixture of styrene, phenyl acetylene and o-xylene with the aid of a palladium or nickel catalyst. In the specific Example hydrogenation is effected with the aid of a palladium catalyst on an alumina carrier.

A drawback of the use of a palladium catalyst is that a palladium catalyst, when used for the hydrogenation of phenyl acetylene in a styrene-containing medium with minor

amounts of impurities, rapidly loses its activity and thus has a short service life. This is a major drawback because it entails high catalyst regeneration costs. Further, regeneration of the catalyst means loss of production or the need to have a second reactor which is put on stream while the catalyst is being regenerated in the first reactor.

The aim of the invention is to provide a catalyst which does not present said drawback or only to a lesser extent.

The invention is characterized in that the catalyst is a supported nickel catalyst with a nickel content of 10-25 wt.%. Surprisingly it has appeared now that in a same styrene-containing medium a nickel catalyst is much less sensitive to impurities and thus has a much longer service life. This is all the more surprising in that a person skilled in the art, relying on his knowledge of catalysts, would not be likely to opt for a nickel catalyst instead of a palladium catalyst, since a nickel catalyst normally has a lower activity and selectivity than a palladium catalyst in the conversion of acetylenes to alkenes (see for instance J.A. Moulijn, P.W.N.M. van Leeuwen and R.A. van Santen, Catalysis, Elsevier, 1993, pp. 180-181).

Further advantages of application of a nickel catalyst are that the price of a nickel catalyst is lower than that of a palladium catalyst and that nickel catalysts are commercially available with a larger catalytically active surface area.

The nickel catalyst applied according to the invention is a supported nickel catalyst. Examples

of suitable carrier materials are: silica, α-, θ- and γ-alumina, zeolites, carbon and oxidic carriers, such as for instance magnesium oxide, titanium oxide and zirconium oxide. Mixtures of different carrier materials can also be used. By preference, θ- and γ-alumina, silica or carbon are used as carrier material. Particular preference is given to θ- or γ-alumina as carrier material, because this is an inert carrier material with a large total surface area and a good poor volume distribution.

The nickel catalyst is synthesized for instance in the following way. The nickel is applied onto the carrier material by impregnating it with a solution of nickel salts. Water is commonly used as solvent. Then the impregnated carrier material is dried and subsequently calcinated at elevated temperature. The nickel oxide thus obtained is then activated on the carrier material through a treatment with hydrogen at elevated temperature. A high degree of dispersion of the nickel on the carrier results in a catalyst with a large catalytically active surface area. The higher the catalytically active surface area in the catalyst, the better the phenyl acetylene is hydrogenated.

For economical and technical reasons the nickel content of the nickel catalyst is kept as low as possible. A nickel catalyst with a higher nickel content is more expensive and when the nickel content becomes higher, the dispersion of the nickel in the catalyst is worse.

The nickel content of the catalyst is

normally 10-25 wt.%. Supported nickel catalysts are commercially available with for instance 10, 15 or 20 wt.% of nickel. The nickel content of the nickel catalyst preferably is 11 to 25 wt.%.

Most preferably the nickel content of the catalyst is more than 11 and less or equal to 20 wt.%.

Besides the nickel the catalyst can also contain minor amounts of other compounds which enhance the activity and selectivity of the catalyst. Examples of such compounds are: chromium, gold, rhodium and ruthenium. The catalyst can also be modified with sulphur-containing compounds.

When its activity in the hydrogenation of phenyl acetylene has declined strongly, the nickel catalyst can be regenerated. Regeneration is effected for instance by treating the contaminated catalyst with steam and air at a high temperature, for instance 300 to 350°C, followed by reduction with hydrogen at the same temperature. If the catalyst is lightly contaminated it can also be regenerated by merely treating it with hydrogen at an elevated temperature of 100-300 °C.

When naphtha, gas condensates and LPG are cracked, cracked petrol is formed. This cracked petrol mainly contains aliphatic and aromatic compounds with 6-9 carbon atoms, including 1-50 wt.% of styrene. Fractionation of this cracked petrol yields a C8 fraction which contains 30-70 wt.% of styrene. When this C8 fraction is extracted with a solvent and then distilled, a styrene-rich fraction is obtained which may contain more than 95 wt.% of styrene. The cracked

petrol, the C8 fraction as well as the styrene-rich fraction can be used as styrene-containing medium.

A styrene-containing medium can also be obtained by means of chemical synthesis. Alkylation of benzene with ethene gives ethyl benzene, which through dehydrogenation can be converted into a styrene-containing medium which besides styrene can also contain ethyl benzene and phenyl acetylene.

The invention is not restricted, however, to the hydrogenation of phenyl acetylene in the above-mentioned styrene-containing media. Styrene-containing media which have been obtained in another way can also be employed.

The styrene-containing media can comprise up to 99.99 wt.% of styrene.

The styrene-containing medium preferably comprises more than 30 wt.% of styrene. By particular preference, the styrene-containing medium is a C8 hydrocarbon fraction which comprises more than 30 wt.% of styrene.

In the hydrogenation of phenyl acetylene in the styrene-containing medium it is preferred for all phenyl acetylene in the styrene-containing medium to be converted to styrene or ethyl benzene, with a limited amount of phenyl acetylene or styrene being hydrogenated to ethyl benzene.

The phenyl acetylene content of a styrene-containing medium is normally between 0.01 and 5 wt.% relative to the styrene present in the styrene-containing medium. During the hydrogenation process according to the invention this content is reduced.

Said content is preferably reduced to less than 100 ppm, by particular preference to less than 10 ppm in the styrene-containing medium.

The process for the hydrogenation of phenyl acetylene in a styrene-containing medium is carried out in a reactor. The catalyst on a support is present in the reactor. The reactor is fed with the styrene-containing medium and hydrogen gas. The hydrogen gas can optionally have been diluted with another, inert gas such as for instance nitrogen gas. The styrene-containing medium and the hydrogen gas can be mixed before being fed to the reactor.

The reactor can be operated as a two-phase or as a three-phase reactor.

If the reactor is operated as a two-phase reactor, then the hydrogen gas that is required for the hydrogenation of the phenyl acetylene is fully dissolved in the styrene-containing medium that is supplied to the reactor.

If the reactor is operated as a three-phase reactor the styrene-containing medium and the hydrogen gas are fed in at the bottom of the reactor and the product is obtained at the top of the reactor. It is also possible to supply the styrene-containing medium and the hydrogen gas at the top of the reactor and to recover the product at the bottom of the reactor. The reactor can also be operated as a countercurrent reactor, with for instance the hydrogen gas being supplied at the bottom of the reactor and the styrene-containing medium at the top. The product is recovered at the bottom of the reactor.

By preference the styrene-containing medium and the hydrogen gas are supplied at the bottom of the reactor, because there is less backmixing then and thus less styrene and phenyl acetylene react further to form ethyl benzene.

The nickel catalyst is preferably present in a fixed bed in the reactor. The styrene-containing medium and the hydrogen gas are contacted with this fixed bed.

A fixed bed is a bed of solid catalyst parts that can have different shapes and can be, for instance, granules, pellets, extrudates, spheres, triloops and qaudruloops. The fixed bed can also consist of a monolith or of miniliths.

The hydrogen pressure in the reactor is usually between 0 and 300.10^5 Pa overpressure, preferably between 0 and 50.10^5 Pa overpressure. Preferably a low pressure is applied, because then the reactor does not have to have a thick wall and is therefore less costly.

The temperature is usually between 0 and 100 °C, preferably between 15 and 50 °C. If the temperature rises above 50 °C, polymerization of styrene occurs during the reaction.

The process according to the invention is preferably carried out with a hydrogen : phenyl acetate molar ratio ≥ 1. By preference this molar ratio is between 1 and 10. For commercial-scale applications this molar ratio is preferably between 1 and 4. The molar ratio is kept as low as possible in order to prevent conversion of styrene and phenyl acetylene into

ethyl benzene.

The average residence time of the styrene-containing medium in the reactor should not be too long, because then more styrene and/or phenyl acetylene react(s) further to ethyl benzene. The average residence time should not be too short either, because then the degree of conversion of phenyl acetylene to styrene is too low. A measure for the average residence time is the liquid hourly space velocity (LHSV).

The process according to the invention is usually carried out with a LHSV of between 0.1 and 100 per hour, preferably between 1 and 10 per hour.

The invention will now be elucidated by means of examples, without being restricted thereto.

Examples:

Example I

A reactor with a capacity of 1 m^3 was completely filled with a fixed bed consisting of a nickel catalyst on θ-alumina. The catalyst contained 15 wt.% of nickel.

A C8 fraction comprising 50 wt.% of styrene, 8 wt.% of ethyl benzene and 0.8 wt.% of phenyl acetylene was supplied to the bottom of this reactor. Hydrogen gas was also supplied to the bottom of the reactor, the hydrogen gas : phenyl acetylene molar ratio being kept between 2 and 3. The LHSV was 4 h^{-1} and the contact time was 15 minutes.

Further data of the reaction are presented in Table 1. The data were registered after different

on-stream times of the reactor. Measurements were carried out after 10, 100 and 220 days.

Comparative Example A

In the reactor of example I a hydrogenation reaction was carried out with a palladium catalyst instead of a nickel catalyst. A palladium catalyst on γ-alumina containing 0.2 wt.% of palladium was used. The other reaction conditions were the same as in example I. The service life of this catalyst was only 10 days. After 10 days the degree of conversion of phenyl acetylene had declined to the point where continuation of the hydrogenation reaction with this catalyst was not sensible any more.

Further data of the reaction are presented in Table 1.

Example II

In the reactor of Example I a hydrogenation reaction was carried out with the catalyst according to Example I after regeneration. The catalyst was regenerated by treating it with steam and air at 300 °C, followed by reduction with hydrogen at the same temperature.

The LHSV was 6 hr^{-1} and the contact time was 10 minutes. The other reaction conditions were the same as in Example I.

Data after different on-stream times of the reactor were registered. Measurements were carried out after 10 and 100 days. Further data of the reaction are presented in Table 1.

Table 1

Example	t (days)	T_{in} (°C)	T_{out} (°C)	ΔT (°C)	X_{ph} (%)	Ph_{out} (ppm)
I	0	28	46	18	99.8	< 10
	10	28	46	18	99.8	< 10
	100	34	49	15	99.7	< 20
	220	39	53	14	99.6	< 30
A	0	20	40	20	99.9	< 10
	10	22	28	6	75.0	200 - 300
II	0	30	45	15	99.8	< 10
	10	30	45	15	99.8	< 10
	100	35	48	13	98.9	100

Explanation of the symbols:

t = time

T_{in} = inlet temperature of the styrene-containing medium

T_{out} = outlet temperature of the styrene-containing medium

ΔT = difference between the inlet and the outlet temperature

X_{ph} = conversion of phenyl acetylene

Ph_{out} = the phenyl acetylene content of the styrene-containing medium leaving the reactor

Example III

A 95 ml reactor was filled with a fixed bed of 70 ml consisting of nickel catalyst on θ-alumina.

The catalyst contained 15 wt.% of nickel.

At the bottom of the reactor a C8 fraction was supplied, containing 50 wt.% of styrene, 8 wt.% of ethyl benzene and 0.8 wt.% of phenyl acetylene.. The LHSV was 5 hr^{-1}, the hydrogen pressure was 3 bar and the inlet temperature was 40 °C. Hydrogen gas was also supplied via the reactor bottom, with a varying hydrogen gas / phenyl acetylene molar ratio, as indicated in Table 2. From Table 2 it appears that at a higher hydrogen gas / phenyl acetylene molar ratio the conversion of phenyl acetylene increases. Some styrene is reacted further to ethyl benzene, however, causing the net styrene yield to decrease a little again.

Example IV

Example III was repeated, using a nickel catalyst on θ-alumina containing 20 wt.% of nickel instead of 15 wt.%. The inlet temperature was 30 °C. The other reaction conditions were the same as in Example III. Hydrogen gas was supplied via the reactor bottom, with a varying hydrogen gas / phenyl acetylene molar ratio, as indicated in Table 2. From Table 2 it appears that at a higher nickel content of the catalyst the same degree of conversion of phenyl acetylene is obtained with a lower hydrogen / phenyl acetylene molar ratio. From this example it also appears that when the hydrogen / phenyl acetylene molar ratio is too high, styrene is also hydrogenated.

Table 2

Example	H_2 / ph (mol/mol)	X_{ph} (%)	S (%)
III	3	98.5	0.3
	5	99.9	0.1
	7	99.9	0.1
IV	1	91	0.4
	2	99.9	0.2
	3	99.9	-0.2

Explanation of the symbols:

X_{ph} = conversion of phenyl acetylene

H_2/ph = molar ratio hydrogen / phenyl acetylene

S = net styrene yield in the medium leaving the reactor relative to the medium supplied to the reactor

Example V

Example III was repeated at elevated temperature and with a LHSV of 5.5 hr^{-1}. At a temperature of 70 °C the conversion of phenyl acetylene was 94% at the start of the experiment. After 5 days the conversion of phenyl acetylene had declined to 30%.

At a temperature of 90 °C the conversion of phenyl acetylene was 100% at the start of the experiment. After 4 days the conversion of phenyl acetylene had declined to 40%.

The strong decline of the conversion of phenyl acetylene is due to formation of polystyrene on the catalyst surface at higher temperatures, resulting in loss of catalyst activity.

C L A I M S

1. Proces for the hydrogenation of phenyl acetylene in a styrene-containing medium with the aid of a catalyst, characterized in that the catalyst is a supported nickel catalyst with a nickel content of 10-25 wt.%.
2. Process according to claim 1, characterized in that the nickel content of the catalyst is 11-25 wt.%.
3. Process according to any one of claims 1-2, characterized in that the carrier material is θ- or γ-alumina.
4. Process according to any one of claims 1-3, characterized in that the catalyst is a fixed-bed catalyst with which the styrene-containing medium and the hydrogen gas are contacted.
5. Process according to any one of claims 1-4, characterized in that the styrene-containing medium and the hydrogen gas are supplied at the bottom of the reactor.
6. Process according to any one of claims 1-5, characterized in that the hydrogen gas / phenyl acetylene molar ratio is 1-10.
7. Process according to any one of claims 1-5, characterized in that the hydrogen gas / phenyl acetylene molar ratio is 1-4.
8. Process according to any one of claims 1-7, characterized in that the phenyl acetylene content of the styrene-containing medium is 0.01-5 wt.%.

9. Process according to any one of claims 1-8, characterized in that the temperature is between 15 and 50 °C.

10. Process according to any one of claims 1-9, characterized in that the LHSV is between 0.1 and 100 per hour.

11. Process according to any one of claims 1-9, characterized in that the LHSV is between 1 and 10 per hour.

12. Process according to any one of claims 1-11, characterized in that the styrene-containing medium contains ≥ 30 wt.% of styrene.

13. Process according to any one of claims 1-11, characterized in that the styrene-containing medium is a C8 hydrocarbon fraction containing ≥ 30 wt.% of styrene.

INTERNATIONAL SEARCH REPORT

Int. ..tional Application No
PCT/NL 99/00245

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C7/167

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8041 Derwent Publications Ltd., London, GB; Class A41, AN 80-72756C XP002086342 & JP 49 007229 A (MARUZEN OIL CO LTD) , 22 January 1974 see abstract & JP 55 035368 B (MARUZEN OIL CO) 12 September 1980 cited in the application --- -/--	1

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 June 1999	07/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Geyt, J

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int .tional Application No
PCT/NL 99/00245

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 75, no. 13, 27 September 1971 Columbus, Ohio, US; abstract no. 88073h, page 319; XP002086341 see abstract & JP 45 036226 B (JAPAN GASOLINE CO) 18 November 1970	1
A	CHEMICAL ABSTRACTS, vol. 112, no. 11, 12 March 1990 Columbus, Ohio, US; abstract no. 98092k, Y. NITTA ET AL: "Partial hydrogenation of phenylacetylene on silica-supported iron catalysts" XP000061086 see abstract & CHEM. EXPRESS, vol. 4, no. 8, 1989, pages 547-550,	1

1